
Kinetic Theory and Thermodynamics

Handout 6:

Clausius' statement of the Second Law

No process is possible whose sole result is the transfer of heat from a colder to a hotter body.

Kelvin's statement of the Second Law

No process is possible whose sole result is the complete conversion of heat into work.

Carnot's theorem

Of all the heat engines working between two given temperatures, none is more efficient than a Carnot engine.

Clausius' theorem

For any closed cycle, $\oint \frac{dQ}{T} \leq 0$ where equality necessarily holds for a reversible cycle.

Application to the Universe:

Law 1: The energy of the Universe is a constant.

Law 2: The entropy of the Universe can only increase.

The entropy form of the first law:

$$\boxed{dU = T dS - p dV}$$

Note that:

$$\begin{aligned} dU &= dW + dQ && \text{always true} \\ dW &= -p dV && \text{only true for reversible changes} \\ dQ &= T dS && \text{only true for reversible changes} \\ dU &= T dS - p dV && \text{always true} \end{aligned}$$

For irreversible changes: $dQ \leq T dS, \quad dW \geq -p dV$

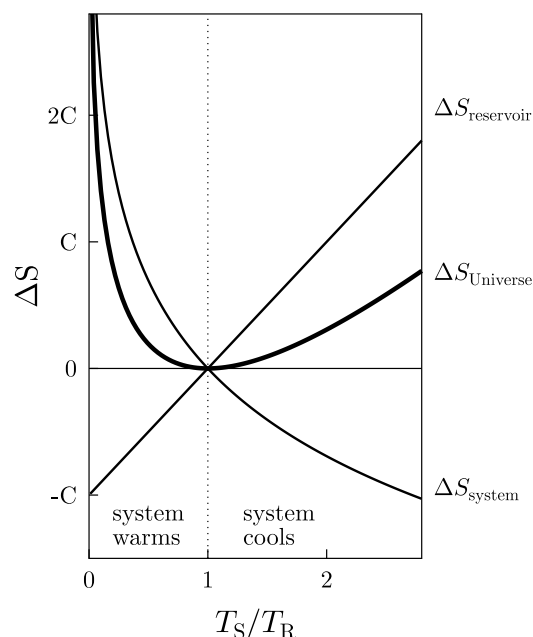
Entropy of the universe

A large reservoir at temperature T_R is placed in thermal contact with a system at temperature T_S . They both end up at temperature T_R . The heat transferred from the reservoir to the system is $C(T_R - T_S)$ where C is the heat capacity of the system.

$$\begin{aligned} \Delta S_{\text{reservoir}} &= \frac{C(T_S - T_R)}{T_R} \\ \Delta S_{\text{system}} &= \int_{T_S}^{T_R} \frac{C dT}{T} = C \ln \frac{T_R}{T_S} \\ \implies \Delta S_{\text{Universe}} &= C \left[\ln \frac{T_R}{T_S} + \frac{T_S}{T_R} - 1 \right] \end{aligned}$$

These expressions are plotted opposite and demonstrate that

$$\Delta S_{\text{Universe}} \geq 0.$$



Thermodynamics potentials

Define the **enthalpy** $H = U + PV$

Define the **Helmholtz function** $F = U - TS$ (sometimes called Helmholtz free energy)

Define the **Gibbs function** $G = H - TS$ (sometimes called the Gibbs free energy).

These are all functions of state, so that one can write down the following exact differentials:

$$\begin{aligned}dU &= TdS - pdV \\dH &= TdS + Vdp \\dF &= -SdT - pdV \\dG &= -SdT + Vdp\end{aligned}$$

Note that each thermodynamic potential has a pair of independent variables:

$$U = U(S, V); \quad H = H(S, p); \quad F = F(T, V); \quad G = G(T, p)$$

These can be used to immediately write down various expressions such as

$$S = - \left(\frac{\partial F}{\partial T} \right)_V, \quad p = - \left(\frac{\partial F}{\partial V} \right)_T$$

This can be used to derive expressions such as:

$$U = F + TS = F - T \left(\frac{\partial F}{\partial T} \right)_V = -T^2 \left(\frac{\partial}{\partial T} \right)_V \left(\frac{F}{T} \right)$$

Maxwell's relations

Following straightforwardly from the exact differentials are the following relations:

$$\begin{aligned}\left(\frac{\partial T}{\partial V} \right)_S &= - \left(\frac{\partial p}{\partial S} \right)_V \\ \left(\frac{\partial T}{\partial p} \right)_S &= \left(\frac{\partial V}{\partial S} \right)_p \\ \left(\frac{\partial S}{\partial V} \right)_T &= \left(\frac{\partial p}{\partial T} \right)_V \\ \left(\frac{\partial S}{\partial p} \right)_T &= - \left(\frac{\partial V}{\partial T} \right)_p\end{aligned}$$

(Don't memorize them, remember how to derive them!)